

EUROPEAN PATENT APPLICATION

Application number: 89308766.8

Int. Cl.⁵: C07C 321/14, C07C 319/14,
C08G 18/38, G02B 1/04

Date of filing: 30.08.89

Priority: 22.12.88 JP 321928/88

Date of publication of application:
25.07.90 Bulletin 90/30

Designated Contracting States:
CH DE FR GB IT LI NL

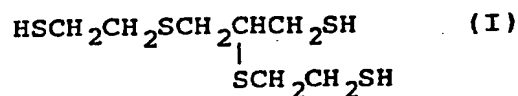
Applicant: MITSUI TOATSU CHEMICALS,
INCORPORATED
2-5, 3-chome, Kasumigaseki
Chiyoda-ku Tokyo(JP)

Inventor: Kanemura, Yoshinobu
2882, Iijimacho Sakae-ku
Yokohama-shi Kanagawa-ken(JP)
Inventor: Sasagawa, Katsuyoshi
1510, Shinyoshidacho Kohoku-ku
Yokohama-shi Kanagawa-ken(JP)
Inventor: Imai, Masao
1-11-10, Hashido Seya-ku
Yokohama-shi Kanagawa-ken(JP)
Inventor: Suzuki, Toshiyuki
4-1-28, Hase
Kamakura-shi Kanagawa-ken(JP)

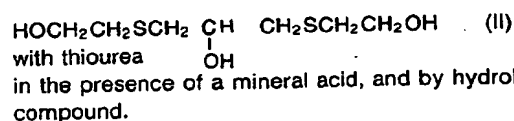
Representative: Stuart, Ian Alexander et al
MEWBURN ELLIS & CO. 2/3 Cursitor Street
London EC4A 1BQ(GB)

A mercapto compound, a high refractive index resin and lens and a process for preparing them.

A compound with the formula



prepared by reacting



A polythiourethane resin can be prepared from this mercapto compound and can be used to make lenses.

A MERCAPTO COMPOUND, A HIGH REFRACTIVE INDEX RESIN AND LENS AND A PROCESS FOR PREPARING THEM

The present invention relates to a mercapto compound, a process for preparing a mercapto compound, a process for preparing a polythiourethane base resin containing the mercapto compound, and a process for preparing plastic lenses containing the resin. The mercapto compound of the invention is useful as a cross-linking agent, a hardener for epoxy resin, a vulcanizing agent, a polymerization modifier, a raw material of plastic resin, an antioxidant, a metal complex forming agent, a biochemical agent and a lubricating oil additive.

A resin presently widely used for plastic lenses is a radical polymerization product of diethyl-2,2-bis(allylcarbonate) (hereinafter abbreviated as DAC). The resin has good impact resistance, is lightweight, has prominent dye affinity, good machinability, and cutting and polishing ability. However, lenses prepared from the resin have a lower refractive index ($n_D = 1.50$) than inorganic lenses ($n_D = 1.52$) have. In order to obtain equivalent optical properties as glass lenses, the center thickness, peripheral thickness and curvature of the lens must be increased, which results in a thick lens.

Other resins useful in preparing plastic lenses having good refractive indexes are polyurethane base resins obtained by reacting isocyanate compounds with hydroxyl compounds such as diethylene glycol (Japanese Patent Laid-Open No. 136601/1982, U.S. Patent No. 4,443,588), with halogen containing hydroxyl compounds such as tetrabromobisphenol-A (Japanese Patent Laid Open No. 164615/1983), with sulfur containing hydroxyl compounds (Japanese Patent Laid-Open Nos. 194401/1985 and 217229/1985, U.S. Patent Nos. 4,680,369 and 4,780,522), and with polythiol compounds (Japanese Patent Laid-Open Nos. 199016/1985, 267316/1987, and 46213/1988, U.S. Patent No. 4,689,387). However, the lenses prepared from these resins exhibit unsatisfactory refractive indexes, although the indexes of these lenses are better than those of lenses prepared from DAC. Further, since these resins are prepared from compounds containing many halogen atoms or aromatic rings to improve the refractive index, lenses containing these resins have disadvantages such as large dispersion of refractive index, poor weatherability and high specific gravity.

Since the indexes of the above lenses are unsatisfactory, and problems in heat resistance during processing such as dyeing, coating and the like exist, and since sulfurous odors of sulfur compounds employed in the prior art may affect the operators' health at the time of preparing lenses, further improved resin compositions are desired.

The present invention may ameliorate or overcome one or more of the problems and disadvantages of prior art resins by providing a novel mercapto compound, a polythiourethane resin containing the mercapto compound, plastic lenses comprising the resin, and processes for producing them.

An object of the invention is to provide a novel mercapto compound having insensible sulfurous odor.

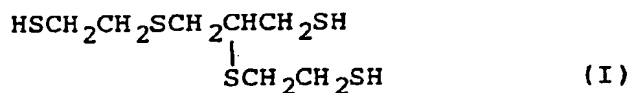
It is desirable to provide a process to prepare the mercapto compound reacting a glycerin derivative or an epihalohydrin with 2-mercapto ethanol to get an triol, and reacting the alcohol with a thiourea to form the mercapto compound.

It is also desirable to provide a colorless and transparent polythiourethane base resin having a high refractive index and low dispersion of refractive index which is suitable for use in producing a lens that is lightweight, excellent in weatherability and exhibits high impact and heat resistance.

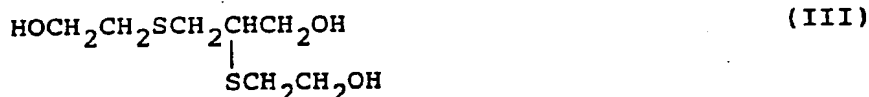
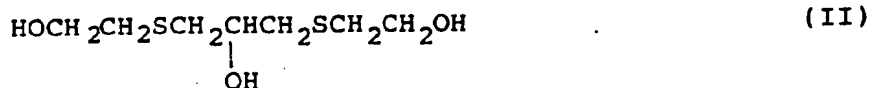
It is also desirable to provide a polythiourethane base lens having high accuracy in the profile of surface and excellent optical properties.

Additional desiderata and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The desiderata and advantages of the invention will be realized and attained by means of the instrumentalities and combinations, particularly pointed out in the appended claims.

The invention provides a mercapto compound of the formula (I) and a process for preparing same



comprising reacting a thio compound with a triol compound of the formula (II) or (III)

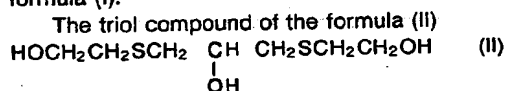


The invention also provides for a polythiourethane base resin comprising reacting the mercapto compound of the formula (I) with one or more ester compounds selected from the group consisting of polyisocyanate compounds, polyisothiocyanate compounds and isothiocyanate compounds having isocyanato groups and a process for producing the resin.

The present invention further provides a lens comprising the resin and a process for producing the lens containing the resin of the invention comprising forming a mixture of the mercapto compound of the formula (I) and one or more ester compounds selected from the group consisting of polyisocyanate compounds, polyisothiocyanate compounds and isothiocyanate compounds having isocyanate groups, pouring the mixture into a mold and polymerizing the mixture to form a lens.

Reference will now be made in detail to embodiments of the invention.

The mercapto compound of the formula (I) can be prepared by reacting a thio compound with the triol compound of the formula (II) or (III) to substitute three hydroxy groups of the triol compound for three mercapto groups. The reaction can be carried out by known hydrolysing methods such as alkali hydrolysis after reacting the triol compound with thiourea in mineral acid. In these circumstances, rearrangement between -OH and -SCH₂CH₂OH of formula (II) takes place to form the mercapto compound represented by formula (I).



can be prepared by reacting a glycerol derivative or epichlorohydrin with 2-mercaptoethanol.

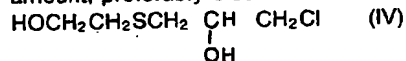
Further, the triol compound of the formula (III) can be prepared by a reaction 2-mercapto ethanol with a glycerine derivative such as 2,3-dibromo-1-propanol.

For example, the mercapto compound of formula (I) can be prepared by adding epichlorohydrin dropwise into an aqueous solution or a lower alcohol, e.g. methanol or ethanol, solution containing 2-mercaptoethanol and a base. In this instance, a reaction temperature between 0° C to 120° C is preferable.

2-Mercaptoethanol is needed more than 2 molar equivalent for epichlorohydrin, and preferably in a range of 2 to 3.

Exemplary suitable base includes a metal hydroxide such as sodium or potassium hydroxide, a metal carbonate such as sodium or potassium carbonate and a tertiary amine such as triethylamine or tributyl amine. Sodium hydroxide is most preferably used because of its inexpensiveness and enough reactivity in molar amounts of more than moles of epichlorohydrin but of less than moles of 2-mercaptoethanol.

To avoid coloring on reactant, the above synthesis is suitably carried out by two steps. For example, at first epichlorohydrin is added dropwise into an aqueous or a lower alcoholic such as of methanol or ethanol solution which contains one to three molar equivalent of 2-mercaptoethanol for epichlorohydrin and catalytic amount, preferably 0.001 to 0.1 molar equivalent, of the base to get a diol compound of formula (IV).



and then 2-mercaptoethanol and the base added to the resulted reactant, respectively to reach two to three and one to two molar equivalent including their respective amounts used at first step to get the triol of formula (II) in second step.

Reacting temperature at first step when strong base is used, is preferable at 0 to 50° C. When the temperature exceeds 50° C, catalytic base acts to form the triol from the diol, and reduces the yield of the diol. In case that of tertiary amine is used at first step, no such a problem arise at a temperature of 50 to 120° C.

Resulted triol compound of formula (II) is reacted with at least three, preferably three to six, molar equivalent of thiourea, in an mineral acid aqueous solution containing at least three, preferably three to twelve, molar equivalent at a temperature of room to refluxing.

Exemplary mineral acid used in above case includes hydrochloric acid, hydrobromic acid, hydroiodic

acid, sulfuric acid and phosphoric acid.

Hydrochloric acid is preferable because of enough reaction velocity and avoiding coloring on product.

Following hydrolysis is carried out by bringing the above resulted reactant to alkali with a metal hydroxide, such as sodium hydroxide, potassium hydroxide, ammonia or a amine, such as triethyl amine, in amount of at least three, preferably three to twelve, molar equivalent at a temperature of room to refluxing.

When adding those alkali to resulted reactant, a temperature of 0 to 50° C is suitable not to cause coloring. The thus produced mercapto compound of formula (I) is purified after extracting by an organic solvent such as toluen by common methods such as washing by acid and water, condensation or filtration, and further distillation is also applicable.

Although the above all steps may practise in air, all steps are suitably practised under nitrogen atmosphere.

The polythiourethane base resin of the present invention is prepared by reacting the mercapto compound of the formula (I) with one or more ester compounds selected from the group consisting of polyisocyanate compounds, polyisothiocyanate compounds and isothiocyanate compounds having isocyanato groups.

Exemplary suitable compounds useful as the polyisocyanate compound in the process of the invention include aliphatic polyisocyanate compounds such as ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, nonamethylene diisocyanate, 2,2-dimethylpentane diisocyanate, 2,2,4-trimethylhexane diisocyanate, decamethylene diisocyanate, butene diisocyanate, 1,3-butadiene-1,4-diisocyanate, 2,4,4-trimethylhexamethylene diisocyanate, 1,6,11-undecane triisocyanate, 1,3,6-hexamethylene triisocyanate, 1,8-diisocyanato-4-isocyanatomethyloctane, 2,5,7-trimethyl-1,8-diisocyanato-5-isocyanatomethyloctane, bis(isocyanatoethyl)-carbonate, bis(isocyanatoethyl)ether, 1,4-butyleneglycol dipropylether- ω,ω -diisocyanate, lysine diisocyanatomethyl ester, lysine triisocyanate, 2-isocyanatoethyl-2,6-diisocyanato hexanoate, 2-isocyanatopropyl-2,6-diisocyanato hexanoate, xylylene diisocyanate, bis(isocyanatoethyl)benzene, bis(isocyanatopropyl)benzene, $\alpha,\alpha,\alpha,\alpha'$ -tetramethylxylylene diisocyanate, bis(isocyanatobutyl)benzene, bis(isocyanatomethyl)naphthalene, bis(isocyanatomethyl)diphenyl ether, bis(isocyanatoethyl)phthalate, mesitylylene triisocyanate and 2,6-di(isocyanatomethyl)furan; alicyclic polyisocyanates such as isophorone diisocyanate, bis(isocyanatomethyl)cyclohexane, dicyclohexylmethane diisocyanate, cyclohexane diisocyanate, methylcyclohexane diisocyanate, dicyclohexyldimethylmethane diisocyanate, 2,2-dimethyl-dicyclohexylmethane diisocyanate, bis(4-isocyanato-n-butylidene)pentaerythritol, dimer acid diisocyanate, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-5-isocyanatomethyl-bicyclo-(2,2,1)-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo-(2,2,1)-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-isocyanatomethylbicyclo-(2,2,1)-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo-(2,2,1)-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-5-(2-isocyanatoethyl)-bicyclo-(2,2,1)-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo-(2,2,1)-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-(2-isocyanatoethyl)-bicyclo-(2,2,1)-heptane and 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo-(2,2,1)-heptane; and aromatic polyisocyanates such as phenylene diisocyanate, tolylene diisocyanate, ethylphenylene diisocyanate, isopropylphenylene diisocyanate, dimethylphenylene diisocyanate, diethylphenylene diisocyanate, diisopropylphenylene diisocyanate, trimethylbenzene triisocyanate, benzene triisocyanate, naphthalene diisocyanate, methylnaphthalene diisocyanate, biphenyl diisocyanate, tolidine diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate, bibenzyl-4,4'-diisocyanate, bis(isocyanatophenyl)ethylene, 3,3'-dimethoxybiphenyl-4,4'-diisocyanate, triphenylmethane triisocyanate, polymeric MDI, naphthalene triisocyanate, diphenylmethane-2,4,4'-triisocyanate, 3-methyldiphenylmethane-4,6,4'-triisocyanate, 4-methyl-diphenylmethane-3,5,2',4',6'-penta-isocyanate, phenylisocyanatomethyl isocyanate, phenylisocyanatoethyl isocyanate, tetrahydronaphthylene diisocyanate, hexahydrobenzene diisocyanate, hexahydrodiphenylmethane-4,4'-diisocyanate, diphenyl ether diisocyanate, ethylene glycol diphenyl ether diisocyanate, 1,3-propylene glycol diphenyl ether diisocyanate, benzophenone diisocyanate, diethylene glycol diphenyl ether diisocyanate, dibenzofuran diisocyanate, carbazole diisocyanate, ethylcarbazole diisocyanate and dichlorocarbazole diisocyanate; sulfur containing aliphatic polyisocyanates such as thiodiethyl diisocyanate, thiodipropyl diisocyanate, thiodihexyl diisocyanate, dimethyl sulfone diisocyanate, dithiodimethyl diisocyanate, dithiodiethyl diisocyanate, and dithiodipropyl diisocyanate; sulfide linkage containing aromatic polyisocyanates such as diphenylsulfide-2,4'-diisocyanate, diphenylsulfide-4,4'-diisocyanate, 3,3'-dimethoxy-4,4'-diisocyanatodibenzyl thioether, bis(4-isocyanatomethylphenyl)sulfide, and 4,4-methoxyphenylthioethyleneglycol-3,3'-diisocyanate; disulfide linkage containing aromatic polyisocyanates such as diphenyldisulfide-4,4'-diisocyanate, 2,2'-dimethyldiphenyldisulfide-5,5'-diisocyanate, 3,3'-dimethyldiphenyldisulfide-5,5'-diisocyanate, 3,3'-dimethyldiphenyldisulfide-6,6'-diisocyanate, 3,3'-dimethyldiphenyldisulfide-5,5'-diisocyanate, 3,3'-dimethyldiphenyldisulfide-6,6'-diisocyanate.

socyanate, 4,4'-dimethyldiphenyldisulfide-5,5'-diisocyanate, 3,3'-dimethoxydiphenyldisulfide-4,4'-diisocyanate, and 4,4'-dimethoxydiphenyldisulfide-3,3'-diisocyanate; sulfone linkage containing aromatic polyisocyanates such as diphenylsulfone-4,4'-diisocyanate, diphenylsulfone-3,3'-diisocyanate, benzidinesulfone-4,4'-diisocyanate, diphenylmethanesulfone-4,4'-diisocyanate, 4-methyldiphenylsulfone-2,4'-diisocyanate, 4,4'-dimethoxy-diphenylsulfone-3,3'-diisocyanate, 3,3'-dimethoxy-4,4'-diisocyanatodibenzyl sulfone, 4,4'-dimethyldiphenylsulfone-3,3'-diisocyanate, 4,4'-di-tert-butylidiphenylsulfone-3,3'-diisocyanate, 4,4'-methoxyphenylethylenedisulfone-3,3'-diisocyanate, and 4,4'-dichlorodiphenylsulfone-3,3'-diisocyanate; sulfonic acid ester linkage containing aromatic polyisocyanates such as 4-methyl-3-isocyanatophenylsulfonyl-4-isocyanatophenol ester and 4-methoxy-3-isocyanatophenylsulfonyl-4-isocyanatophenol ester; sulfonamide linkage containing aromatic polyisocyanates such as 4-methyl-3-isocyanatophenylsulfonylanilide-3-methyl-4-isocyanate, diphenylsulfonylethylenediamine-4,4'-diisocyanate, 4,4'-methoxyphenylsulfonylethylenediamine-3,3'-diisocyanate, and 4-methyl-3-isocyanatophenylsulfonylanilide-4-methyl-3-isocyanate; sulfur containing heterocyclic compounds such as thiophene-2,5-diisocyanate; and 1,4-dithian-2,5-diisocyanate.

In addition, halogen-substituted compounds such as chlorine-substituted and bromine-substituted compounds, alkyl-substituted compounds, alkoxy-substituted compounds, nitro-substituted compounds, polyvalent alcohol-modified prepolymer type compounds, carbodiimido-modified compounds, urea-modified compounds, biuret-modified compounds of the above polyisocyanate compounds, and products of dimerization and trimerization reactions of these polyisocyanate compounds may be employed.

Exemplary suitable polyisothiocyanate compounds useful in the process of invention include such compounds having two or more functional isothiocyanato groups in the molecule, and may also contain a sulfur atom, such as aliphatic polyisothiocyanate compounds, for example, 1,2-diisothiocyanatoethane, 1,3-diisothiocyanatopropane, 1,4-diisothiocyanatobutane, 1,6-diisothiocyanatohexane, p-phenylenediisopropylidenediisothiocyanate; alicyclic polyisothiocyanate compounds such as cyclohexanediisothiocyanate; aromatic polyisothiocyanates such as 1,2-diisothiocyanatobenzene, 1,3-diisothiocyanatobenzene, 1,4-diisothiocyanatobenzene, 2,4-diisothiocyanatotoluene, 2,5-diisothiocyanato-m-xylene, 4,4'-diisothiocyanato-1,1'-biphenyl, 1,1'-methylenebis(4-isothiocyanatophenyl), 1,1'-methylenebis(4-isothiocyanato-2-methylphenyl), 1,1'-methylenebis(4-isothiocyanato-3-methylphenyl), 1,1'-(1,2-ethanediyl)-bis(4-isothiocyanatophenyl), 4,4'-diisothiocyanatobenzophenone, 4,4'-diisothiocyanato-3,3'-dimethylbenzophenone, benzanilide-3,4'-diisothiocyanate, diphenylether-4,4'-diisothiocyanate, diphenylamine-4,4'-diisothiocyanate; isothiocyanates containing a heterocyclic ring such as 2,4,6-trisothiocyanato-1,3,5-triazine; carbonylisothiocyanates such as hexanedioyldiisothiocyanate, nonane dioyldiisothiocyanate, carbonic diisothiocyanate, 1,3-benzenedicarbonyl diisothiocyanate, 1,4-benzenedicarbonyldiisothiocyanate, (2,4'-bipyridyl)-4,4'-dicarbonyldiisothiocyanate.

Exemplary compounds suitable for use as a polyisothiocyanate compound containing at least two isothiocyanato groups and at least one sulfur atom in the process of the invention include sulfur-containing aliphatic isothiocyanate compounds such as thiobis(3-isothiocyanatopropane), thiobis(2-isothiocyanatoethane), dithiobis(2-isothiocyanatoethane); sulfur-containing aromatic isothiocyanate such as 1-isothiocyanato-4-[(2-isothiocyanato)sulfonyl]benzene, thiobis(4-isothiocyanatophenyl), sulfonylbis(4-isothiocyanatophenyl), sulfinylbis(4-isothiocyanatophenyl), 4-isothiocyanato-1-[(4-isothiocyanatophenyl)sulfonyl]-2-methoxybenzene, 4-methyl-3-isothiocyanatobenzenesulfonyl-4-isothiocyanatophenylester, 4-methyl-3-isothiocyanatobenzenesulfonylanilide-3-methyl-4-isothiocyanate; sulfur containing heterocyclic compounds such as thiophene-2,5-diisothiocyanate and 1,4-dithian-2,5-diisothiocyanate.

In addition, halogen-substituted compounds such as chlorine-substituted and bromine-substituted compounds, alkyl-substituted compounds, alkoxy-substituted compounds, nitro-substituted compounds, polyvalent alcohol-modified prepolymer type compounds, carbodiimido-modified compounds, urea-modified compounds, biuret-modified compounds of the above polyisothiocyanate compounds, and products of dimerization and trimerization reactions of these polyisothiocyanate compounds may be employed.

Exemplary suitable compounds useful as isothiocyanate compounds having isocyanato groups in the process of the invention include aliphatic or alicyclic compounds such as 1-isocyanato-3-isothiocyanatopropane, 1-isocyanato-5-isothiocyanatopentane, 1-isocyanato-6-isothiocyanatohexane, isothiocyanatocarbonylisocyanate, 1-isocyanato-4-isothiocyanatocyclohexane; aromatic compounds such as 1-isocyanato-4-isothiocyanato benzene and 4-methyl-3-isocyanato-1-isothiocyanato benzene; heterocyclic compounds such as 2-isocyanato-4,6-diisothiocyanato-1,3,5-triazine; compounds having a sulfur atom and an additional isothiocyanato group such as 4-isocyanato-4-isothiocyanato diphenyl sulfide and isocyanato-2'-isothiocyanatodiethylidisulfide.

Halogen-substituted compounds such as chlorine substituted and bromine-substituted compounds, alkyl-substituted compounds, and alkoxy-substituted compounds, nitro-substituted compounds, polyvalent

alcohol-modified prepolymer type compounds, carbodiimido-modified compounds, urea-modified compounds, biuret-modified compounds of the above isothiocyanate compounds, and products of dimerization and trimerization reactions of these isothiocyanate compounds may also be employed.

The ester compounds may be used alone or in combination as a mixture. The proportion of the ester compounds to the mercapto compound of the formula (I) is a mole ratio of from about 0.5 to about 3.0 moles of functional (NCO + NCS) group per mole of functional mercapto group, preferably from about 0.5 to about 1.5 moles of functional (NCO + NCS) group per mole of functional mercapto group.

In the plastic lens of the present invention, an S-alkyl thiocarbamic acid ester resin or a dithiourethane resin may be employed as a raw material, and therefore in the lens an S-alkyl thiocarbamic acid ester bond is present between an isocyanato group and a mercapto group, or a dithiourethane bond is present between an allophanate bond, a urea bond, or a biuret bond. However, the plastic lens of the invention may also contain an isothiocyanato group and a mercapto group. For example, it may be desirable to further react the isocyanato group with the S-alkyl thiocarbamic acid ester bond, or to react the isothiocyanato group with the dithiourethane bond to increase the cross-link density. Such a reaction may be carried out at a temperature of at least 100°C and the isocyanato or isothiocyanato component should be used in an excess amount. Alternatively, an amine compound or the like may also be used to produce a urea bond or a biuret bond. When the isocyanate compound and/or isothiocyanate compound is reacted with a compound other than the mercapto compound, attention should be paid to coloring.

Various additives may be added to the above raw materials. Exemplary suitable additives include an internal mold releasing agent, a chain extender, a cross-linking agent, a light stabilizer, an ultraviolet absorber, an anti-oxidant, an oil-soluble dye and a filler.

The reaction rate may be adjusted to a desired level by adding a known reaction catalyst useful in the manufacture of a polyurethane.

The plastic lens of the present invention can be prepared by cast polymerization. A mercapto compound of the formula (I) and one or more ester compounds are mixed to form a mixture. The mixture is then poured into a mold, degasified if necessary, followed by polymerization. To facilitate releasing the lens from a mold after polymerization, the mold can be treated with a known release method.

The resin of the present invention does not give workers an unpleasant feeling from sulfurous odors of its monomers during treating, and during and after processing.

The resin has a very low dispersion property, a high refractive index, is excellent in heat resistance and is colorless and transparent. The resin is also lightweight, has excellent weatherability and impact resistance.

The resin is suitable for use as optical element material such as eyeglass lenses and camera lenses, and for glazing materials, paint and bonding materials.

Moreover, the plastic lenses of the present invention can be subjected to physical and chemical treatment such as surface abrasion treatment, anti-static treatment, hard coat treatment, non-reflective coat treatment, coloring treatment and dimming treatment for prevention of reflection, enhancement of hardness, improvement of abrasion resistance and chemical resistance, prevention of turbidity, supply of fashionability, and the like.

The invention will be further described and clarified by the following examples and comparative examples which are intended to be purely exemplary of the invention.

The performance tests of the resins and lenses, specifically the tests of refractive index, Abbe's number, weatherability, appearance and odor were carried out by the following procedure:

Refractive index and Abbe's number:

Measured at 20°C with a Pulfrich refractometer.

Weatherability:

A lens resin was set in a weatherometer equipped with a sunshine carbon arc lamp. The lens was taken out after 20 hours and its hue was compared with that of a lens resin before the test. Evaluation was classified into no change (O), slight yellowing (Δ), and yellowing (X).

Appearance:

Evaluation was conducted by visual observation.

Odor:

Evaluation has classified into little smelling (0), slight smelling (Δ) and strong smelling (X) of sulfurous odor upon mixing the monomer.

Heat resistance:

Test pieces were separately heated at a rate of 2.5 °C/min under a load of 5 g by means of a "Thermomechanical Analyzer" (manufactured by Perkin-Elmer Company, U.S.A.) to measure their heat-distortion starting temperatures.

Example 1

Synthesis of the mercapto compound of formula (I):

53.2 g (0.681 mol) of 2-mercapto ethanol and 27.2 g (0.680 mol) of sodium hydroxide were dissolved in 200 ml of ethanol and homogenized. 30.0 g (0.324 mol) of epichlorohydrin were added dropwise to the ethanol solution while maintaining an inner temperature of 15 °C.

The mixture was heated to 50 °C and stirred for one hour. The reaction mixture was cooled at room temperature and 40.5 g (0.399 mol) of hydrochloric acid (36%) were added to form a precipitate. The salt precipitated was separated by filtration with suction. The filtrate was concentrated under reduced pressure and 70.6 g of 1,3-bis(2-hydroxyethylthio)-2-propanol (formula (II) compound) were obtained as a colorless and viscous liquid.

The product was dissolved in 203 g (2.00 mol) of hydrochloric aqueous solution (36%) and 92.6 g (1.22 mol) of thiourea were added to the solution. The solution was heated and stirred for six hours at 110 °C.

The solution was cooled to room temperature, and 195 g (2.44 mol) of sodium hydroxide 50% aqueous solution were added while keeping at 20 to 40 °C, heated and stirred for 30 minutes at 110 °C.

The solution was cooled to room temperature and 100 ml of toluene were added for separatory extraction. The toluene phase was washed with 100 ml of hydrochloric acid 5% aqueous solution and with 100 ml of water two times. The toluene solution obtained was dried by anhydrous sodium sulfate. 75.6 g (0.290 mol) of 1,2-bis(2-mercaptoethylthio)-3-mercaptopropane (formula (I) compound) were obtained as a colorless and viscous liquid (APHA 15) after concentration.

Results of elemental analysis and NMR analysis are as follows:

Elemental analysis (as C ₇ H ₁₆ S ₅):			
	C	H	S
Found (%)	32.12	6.19	61.69
Calculated (%)	32.27	6.19	61.53

¹H NMR analysis (in CDCl₃):

$\delta_{\text{ppm}} =$
 1.74 - 1.91 (m, 3H, -SH)
 2.70 - 3.00 (m, 13H, $\overline{\text{CH}}$)
¹³C NMR (in CDCl₃)

$\delta_{\text{ppm}} =$
 24.7 -S-CH₂-CH₂-SH
 24.9 -S-CH₂- $\overline{\text{CH}_2}$ -SH
 28.6 -S-CH₂- $\overline{\text{CH}}$ -CH₂-SH
 |
 S-

35.4 -SCH₂CH₂SH36.0 -SCH₂CH₂SH36.8 -SCH₂ CH CH₂SH

5 48.7 -SCH₂ $\begin{array}{c} \text{CH} \\ | \\ \text{S}- \\ | \\ \text{C} \\ | \\ \text{S}- \end{array}$ CH₂SH

10 Example 2

88.7 g (1.14 mol) 2-mercapto ethanol were added dropwise into 50.4 g (0.567 mol) of sodium hydroxide aqueous solution (45%) and homogenized. 50.5 g (0.546 mol) of epichlorohydrin were added dropwise to the homogenized solution extending over 1.5 hours, then kept at 112° C for 0.5 hours with stirring.

15 After the reaction mixture cooled to room temperature, 270 g of concentrated hydrochloric acid (36%, 2.66 mol) and 154 g (2.02 mol) of thiourea were added to the mixture, and stirred for 1.5 hours at 112° C.

288 g of aqueous sodium hydroxide (45%, 3.24 mol) was added while keeping at 20 to 35° C dropwise to the reaction mixture extending for 0.5 hours, and then stirred at 110° C for 1.5 hours.

20 The reaction mixture was then cooled at room temperature, 200 ml of water and 250 ml of toluene were added for separatory extraction. The toluene phase was washed with 50 ml of hydrochloric acid (36%) and with 200 ml of water three times, then concentrated in vacuo and distilled (b.p 185 - 205° C/0.4 Torr) and 105.8 g (0.406 mol) of 1,2-bis(2-mercaptoethylthio)-3-mercapto propane (Formula (I) compound) were obtained as a viscous liquid (APHA 10).

Results of elemental analysis and NMR analysis were same as of Example 1.

25

Example 3

84.4 g (1.08 mol) of 2-mercapto ethanol were added to 0.8 g (0.001 mol) of 48.7% sodium hydroxide and homogenized, and then 50.0 g (0.540 mol) of epichlorohydrin was added to the solution dropwise below 40° C extending over 0.5 hours, further kept the mixture stirring for 0.5 hours.

44.4 g (0.541 mol) of aqueous sodium hydroxide (48.7%) were added dropwise to the reaction mixture extending for 0.5 hours, and cooled with stirring to room temperature for 0.5 hours, 313 g (3.09 mol) of hydrochloric acid (36%) and 123.4 g (1.62 mol) of thiourea were added to the reaction mixture and stirred 35 1.5 hours at 112° C.

After cooling to room temperature, 254 g (3.09 mol) of aqueous sodium hydroxide (48.7%) was added to the reaction mixture at a range of temperature 25 to 35° C, then stirred and heated at 110° C for 1.5 hours.

40 The reaction mixture was cooled to room temperature and 150 g of water and 180 g of toluene were added for separatory extraction. The toluene phase was washed with 150 g of hydrochloric acid (18%) and with 30 ml of water three times, then concentrated and distilled in vacuo (120° C/2 Torr, 2 hours) followed by a filtration with a filter (one micron pore size) to get 129 g (0.495 mol) of 1,2-bis(2-mercaptoethylthio)-3-mercaptopropane (formula (I) compound) as a viscous liquid (APHA 10).

Results of elemental analysis and NMR analysis were same as of Example 1.

45

Example 4

84.4 g (1.08 mol) of 2-mercaptoethanol was added to 1.0 g (0.005 mol) of tributylamine, and 50.0 g (0.540 mol) of epichlorohydrin was added dropwise to the solution extending over 0.5 hours, and stirred further for 0.5 hours.

Then while cooling the mixture to a range of 40 to 70° C, 44.4 g (0.541 mol) of aqueous sodium hydroxide (48.7%) was added extending over 0.5 hours dropwise into the mixture.

55 After stirring for 0.5 hours, the mixture was cooled to room temperature and 313.1 g (3.09 mol) of hydrochloric acid (36%) and 123.4 g (1.62 mol) of thiourea, were added to the mixture then stirred for 1.5 hours at 112° C.

The reaction mixture was then cooled at room temperature, 254 g (3.09 mol) of aqueous sodium hydroxide (48.7%) was added while keeping at 25 to 35° C and stirred at 110° C for 1.5 hours.

Again after cooled the reaction mixture to room temperature, 150 ml of water and 180 ml of toluene were added for separatory extraction. The toluene phase was washed with 150 g of hydrochloric acid (18%) and with 30 g of water three times, then concentrated and distilled in vacuo (120 °C/2 Torr, 2 hours), followed by a filtration with a filter (one micron pore size) to get 125 g (0.480 mol) of 1,2-bis(2-mercaptoethylthio)-3-mercaptopropane (formula (I) compound) as a viscous liquid (APHA 10).
Results of elemental and NMR analysis were same to as Example 1.

Example 5

44.4 g (0.541 mol) of aqueous sodium hydroxide (48.7%) were added to a mixture of 84.4 g (1.08 mol) of 2-mercapto ethanol with 50.0 g (0.540 mol) epichlorohydrin, at a range between room temperature to 60 °C extending over one hour, further stirred the mixture at 80 °C for 0.5 hours.

After cooling to room temperature, 313 g (3.09 mol) of hydrochloric acid (36%) and 123.4 g (1.62 mol) of thiourea were added to the reaction mixture and stirred at 112 °C for 1.5 hours.

The reaction mixture was cooled again to room temperature, and 254 g (3.09 mol) of aqueous sodium hydroxide (48.7%) was added to the reaction mixture at a range of 25 °C to 35 °C, and stirred at 110 °C for 1.5 hours.

After cooling to room temperature, 150 g of water and 180 g of toluene were added to the reaction mixture for separatory extraction. The toluene phase was washed with 150 g of hydrochloric acid (18%) and with 30 g of water three times, then concentrated and distilled in vacuo (120 °C/2 Torr, 2 hours), filtered by a filter (pore size one micron) to get 122 g (0.468 mol) of 1,2-bis(2-mercaptoethylthio)-3-mercaptopropane (Formula (I) compound) as a viscous liquid (APHA 15), with the same elemental and NMR analysis data of Example 1.

Example 6

735 g (1.50 mol) of sulfuric acid (20%) substituted for 270 g (2.66 mol) of hydrochloric acid (36%) in Example 2.

As a result, 102 g (0.392 mol) of 1,2-bis-(2-mercaptoethylthio)-3-mercaptopropane (Formula (I) compound) with the same data on elemental and NMR analysis of Example 1.

Example 7

327 g (1.00 mol) of phosphoric acid (30%) substituted for 270 g (2.66 mol) of hydrochloric acid (36%) in Example 2.

100 g (0.384 mol) of 1,2-bis-(2-mercaptoethylthio)-3-mercaptopropane (Formula (I) compound) resulted with the same data on elemental and NMR analysis of Example 1.

Example 8

53.2 g (0.681 mol) of 2-mercaptoethanol and 27.2 g (0.680 mol) of sodium hydroxide were dissolved into 200 ml of ethanol and homogenized, 70.0 g (0.324 mol) of 2,3-dibromo-1-propanol were added dropwise to the ethanol solution while keeping an inner temperature of 15 °C.

The mixture was heated to 50 °C and stirred for one hour, followed by a cooling to room temperature to form a precipitate. The salt precipitated was separated by filtration with suction. The filtrate was concentrated under reduced pressure and 71.3 g of a mixture of 1,3-bis(2-hydroxyethylthio)-2-propanol (Formula (II) compound) with 1,2-bis-(2-hydroxyethylthio)-3-propanol (Formula (III) compound) as a colorless and viscous liquid.

The mixture was dissolved in 203 g (2.00 mol) of hydrochloric acid (36%) and 92.6 g (1.22 mol) of thiourea were added to the solution. The solution was cooled to room temperature, and 195 g (2.44 mol) of sodium hydroxide 50% aqueous solution were added while keeping at 20 to 40 °C, heated and stirred for 30 minutes at 110 °C.

The solution was cooled to room temperature and 100 ml of toluene were added for separatory extraction. The toluene phase was washed with 100 ml of hydrochloric acid 5% aqueous solution and with

EP 0 378 895 A1

100 ml of water two times. The toluene solution obtained was dried by anhydrous sodium sulfate. 75.6 g (0.290 mol) of 1,2-bis(2-mercaptoethylthio)-3-mercaptopropane (Formula (I) compound) were obtained as a colorless and viscous liquid (APHA 15) after concentration.

Results of elemental analysis and NMR analysis are as follows:

Elemental analysis (as C ₇ H ₁₆ S ₅):			
	C	H	S
Found (%)	32.14	6.17	61.69
Calculated (%)	32.27	6.19	61.53

¹H NMR analysis (in CDCl₃):

δ_{ppm} =

1.74 - 1.91 (m, 3H, -SH)

2.70 - 3.00 (m, 13H, CH)

¹³C NMR (in CDCl₃)

δ_{ppm} =

24.7 -SCH₂CH₂SH

24.9 -SCH₂CH₂SH.

28.6 -SCH₂-CH-CH₂SH

35.4 -SCH₂CH₂SH

36.0 -SCH₂CH₂SH

36.8 -SCH₂-CH-CH₂SH

48.7 -SCH₂-CH-CH₂SH

Example 9

A mixture of 87 g of the compound obtained in Example 1 and 94 g of m-xylylene diisocyanate were homogenized and were poured into a mold composed of a glass mold and gasket, and then were heated and cured. The resin produced was colorless and transparent, excellent in high impact resistance, had a refractive index *n*_D20 of 1.66 and Abbe's number *v*_D of 33 and a heat distortion starting temperature of 98° C.

Examples 10-28 and Comparative Examples 1 to 11

Following the procedure of Example 9, lenses were prepared in composition ratios shown in Table 1. The results of performance tests are set forth in Table 1.

TABLE 1

Example	Ester Compound (Polyisothiocyanate, amount by mole)	Polythiol (mole)	Refractive index	Abbe's Number	Weather- ability	Appearance	Odor	Heat resistance (°C)
Example 9	m-Xylylenediisocyanate (0.5)	1,2-Bis-(2-mercaptoethylthio)- 3-mercaptopropane (Compound of formula (1))(0.33)	1.66	33	○	Colorless and transparent	○	98
Example 10	Isophoronediiisocyanate (0.5)	"	1.60	40	○	"	○	142
Example 11	1,4-bis(isocyanate methyl) cyclohexane (0.5)	"	1.62	39	○	"	○	
Example 12	OCN-(CH ₂) ₆ -NCO (0.5)	"	1.62	39	○	"	○	
Example 13	m-Xylylenediisocyanate (0.4) Tolylenediisocyanate (0.1)	"	1.67	30	○	"	○	
Example 14	Thiodiethyldiisocyanate (0.5)	"	1.65	34	○	"	○	
Example 15	Dithiodiethyldiisocyanate (0.5)	"	1.67	33	○	"	○	
Example 16	Dithiodipropyldiiso- cyanate (0.5)	"	1.65	34	○	"	○	

- to be cont'd. -

Table 1 (Cont'd.)

Comparative example 1	m-Xylylenediisocyanate (0.5)	Pentaerythritol-tetrakis(3-mercaptopropionate) (0.25)	1.59	36	○	Colorless and transparent	x	84
" 2	"	Tetrabromobisphenol A (0.5)	1.61	27	△	Transparent slightly yellowish	○	
" 3	Hexamethylenediisocyanate (0.5)	1,4-Butanediol (0.5)	1.50	55	○	Transparent Colorless	○	
" 4	Isophoronediiisocyanate (0.5)	Pentaerythritoltetrakis(3-mercaptopropionate) (0.25)	1.54	47	○	"	x	117
Example 17	$\text{SCN}(\text{CH}_2)_6\text{NCS}$ (0.5)	1,2-Bis-(2-mercaptoethylthio)-3-mercaptopropene (Compound of formula (I)) (0.33)	1.70		○	"	○	
Example 18	$\text{SCN}-\text{C}_6\text{H}_4-\text{S}-\text{S}-\text{C}_6\text{H}_4-\text{NCS}$ (0.5)	" (0.33)	1.77		○	"	○	
Example 19	$\text{S}(\text{CH}_2)_2\text{NCS})_2$ (0.5)	" (0.33)	1.73		○	"	○	
Example 20	$\text{SCN}-\text{C}_6\text{H}_4-\text{NCS}$ (0.5)	" (0.33)	1.75		○	"	○	
Comparative Example 5	m-Xylylenediisocyanate (0.5)	Pentaerythritoltetrakis-(thioglycolate) (0.33)	1.60	34	○	"	x	
" 6	" (0.5)	Ethanedithiol (0.5)	1.65		○	"	x	
" 7	" (0.5)	Xylylenedithiol (0.5)	1.66	29	○	"	x	
" 8	" (0.5)	1,3-Propanedithiol (0.5)	1.64		○	"	x	

Table 1 (Cont'd.)




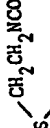
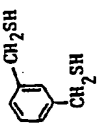
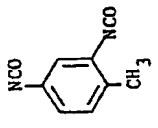
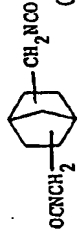
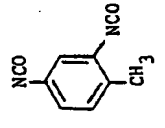
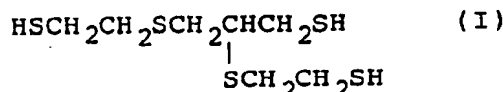
	Ester Compound (Isothiocyanate compound having isocyanate group, mole)	Polythiol (mole)	Refractive index	Abbe's Number	Weather- ability	Appearance	Odor	Heat resistance (°C)
Example 21	$\text{OCN}(\text{CH}_2)_6\text{NCS}$ (0.5)	1,2-Bis-(2-mercaptoethylthio)- 3-mercaptopropane (Compound of formula (I)) (0.33)	1.67		○	Transparent Colorless	○	
Example 22	OCN -  -NCS (0.5)	" (0.33)	1.72		○	"	○	
Example 23	OCN -  -NCS (0.5)	" (0.33)	1.68		○	"	○	
Example 24	OCN -  -NCS (0.5)	" (0.33)	1.74		○	"	○	
Example 25	S -  -NCS (0.5)	" (0.33)	1.70		○	"	○	
Example 26	S - $\text{CH}_2\text{CH}_2\text{NCO}$ S - $\text{CH}_2\text{CH}_2\text{NCS}$ (0.5)	" (0.33)	1.71		○	"	○	
Comparative example 9	S - $\text{CH}_2\text{CH}_2\text{NCO}$ S - $\text{CH}_2\text{CH}_2\text{NCS}$ (0.5)	$\text{C}(\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH})_4$ (0.25)	1.71		○	"	X	
Comparative Example 10	" (0.5)	 (0.5)	1.71		○	"	X	

Table 1 (Cont'd.)

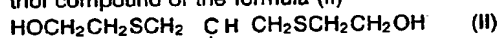
	Ester Compound (Polyisothiocyanate, amount by mole)	Polythiol (mole)	Refractive index	Abbe's Number	Weather- ability	Appearance	Odor	Heat resistance (°C)
Example 27	 (0.5)	1,2-Bis-(2-mercaptoethylthio)- 3-mercaptopropane (Compound of formula (I)) (0.33)	1.69	26	○	Transparent Colorless	○	140
Example 28	 (0.5)	" (0.33)	1.62	41	○	"	○	118
Comparative Example 11	 (0.5)	Pentaerythritol tetrakis- (3-mercaptopropionate) (0.25)	1.62	32	X	Pale yellowish transparent	X	125

Claims

1. A mercapto compound of the formula (I)

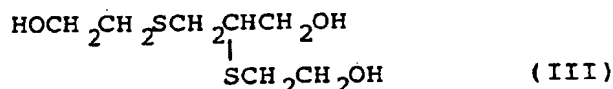


2. A process for preparing the mercapto compound of the formula (I) comprising reacting thiourea and a triol compound of the formula (II)



in the presence of a mineral acid, and hydrolysing the reaction mixture with a base to form the mercapto compound.

3. A process for preparing the mercapto compound of the formula (I) comprising reacting thiourea and a triol compound of the formula (III)



in the presence of a mineral acid, and hydrolysing the reaction mixture with a base to form the mercapto compound.

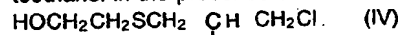
4. A process for preparing the mercapto compound of formula (I) comprising getting the triol compound of formula (II) by reacting epihalohydrin with 2-mercapto ethanol in the presence of a base, reacting the triol compound with thiourea in the presence of a mineral acid and hydrolysing the reactant with a base to form the mercapto compound.

5. The process of claim 4 wherein the epihalohydrin is epichlorohydrine.

6. A process for preparing the mercapto compound of the formula (I) comprising getting a mixture of triol compounds of the formula (II) and (III) by reacting 2,3-dihalogeno-1-propanol with 2-mercaptoethanol in the presence of a base, reacting the mixture with thiourea in the presence of a mineral acid and hydrolysing the reactant with a base to form the mercapto compound.

7. The process of claim 6 wherein the 2,3-dihalogeno-1-propanol is 2,3-dibromo-1-propanol.

8. A process for preparing the mercapto compound of the formula (I) claimed in claim 5 comprising reacting one chemical equivalent of epichlorohydrin with one to three chemical equivalent of 2-mercaptoethanol in the presence of 0.001 to 0.1 chemical equivalent of a base to form a diol of formula (IV)



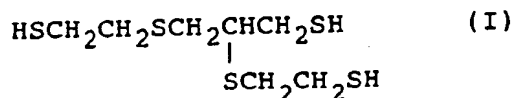
reacting the diol with 2-mercaptoethanol which is increased to reach totally to two to three chemical equivalent and a base which is increased to reach totally to one to two chemical equivalent in alkaline pH to form the triol of formula (II).

9. A process of any one of claims 2 to 8 wherein the mineral acid is hydrochloric acid.

10. A process of any one of claims 2 to 8 wherein the hydrolysing is carried out at a temperature of 0 to 50 °C.

11. The process of claim 8 wherein forming the diol of formula (IV) is carried out at a temperature of 0 to 50 °C.

12. A polythiourethane base resin comprising reacting a mercapto compound of the formula (I)



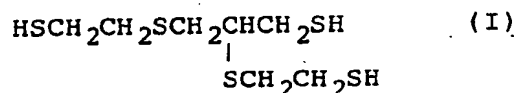
5 with at least one ester compound selected from the group consisting of polyisocyanate compounds, polyisothiocyanate compounds and isothiocyanate compounds having a isocyanato groups.

13. The resin of claim 12 wherein the mole ratio of said at least one ester compound to said mercapto
10 compound is from about 0.5 to about 3.0 moles of functional (NCO+NCS) groups per mole of functional mercapto group.

14. The process for preparing the resin of claim 12 wherein the reaction is carried out by heating and curing.

15. The process for preparing the resin of claim 13 wherein the reaction is carried out by heating and
15 curing.

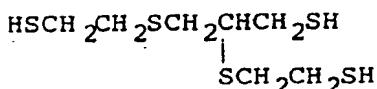
16. A plastic lens comprising reacting a mercapto compound of the formula (I)



20 with at least one ester compound selected from the group consisting of polyisocyanate compounds, polyisothiocyanate compounds and isothiocyanate compounds having a isocyanato groups.

25 17. The lens of claim 16 wherein the mole ratio of said at least one ester compound to said mercapto compound is from about 0.5 to about 3.0 moles of functional (NCO+NCS) groups per mole of functional mercapto group.

18. A process for producing a plastic lens comprising mixing a mercapto compound of the formula (I)



35 with at least one ester compound selected from the group consisting of polyisocyanate compounds, polyisothiocyanate compounds and isothiocyanate compounds having a isocyanato groups to form a mixture; casting and polymerizing the mixture to form a plastic lens.

40 19. The process of claim 18 wherein the mole ratio of said at least one ester compound to said mercapto compound is from about 0.5 to about 3.0 moles of functional (NCO+NCS) groups per mole of functional mercapto group.

20. The process of claim 18 comprising adding to said mixture at least one compound selected from the group consisting of internal mold release agents, chain extenders, crosslinking agents, light stabilizers, ultraviolet absorbers, anti-oxidants, oil-soluble dyes and fillers.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 30 8766

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	CHEMICAL ABSTRACTS, vol. 104, no. 7, February 1986, page 488, abstract no. 50541p, Columbus, Ohio, US; & JP-A-60 161 962 (NISSO PETROCHEMICAL INDUSTRIES CO., LTD) 23-08-1985 ---	2,3	C 07 C 321/14 C 07 C 319/14 C 08 G 18/38 G 02 B 1/04
Y	CHEMICAL ABSTRACTS, vol. 104, no. 15, April 1986, page 663, abstract no. 129491f, Columbus, Ohio, US; & JP-A-60 158 163 (NISSO PETROCHEMICAL INDUSTRIES CO, LTD) 19-08-1985 -----	2,3	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 07 C 321/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27-03-1990	Examiner VAN GEYT J.J.A.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.